Novel Binders and Methods for Agglomeration of Ore

Semiannual Technical Progress Report

Reporting Period Start Date: April 2005
Reporting Period End Date: September 2005

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Report Issued October 2005
DOE award # DE-FC26-03NT41924
Budget Period 2

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Abstract

Many metal extraction operations, such as leaching of copper, leaching of precious metals, and reduction of metal oxides to metal in high-temperature furnaces, require agglomeration of ore to ensure that reactive liquids or gases are evenly distributed throughout the ore being processed. Agglomeration of ore into coarse, porous masses achieves this even distribution of fluids by preventing fine particles from migrating and clogging the spaces and channels between the larger ore particles. Binders are critically necessary to produce agglomerates that will not break down during processing. However, for many important metal extraction processes there are no binders known that will work satisfactorily at a reasonable cost. A primary example of this is copper heap leaching, where there are no binders currently encountered in this acidic environment process. As a result, operators of many facilities see a large loss of process efficiency due to their inability to take advantage of agglomeration. The large quantities of ore that must be handled in metal extraction processes also means that the binder must be inexpensive and useful at low dosages to be economical. The acid-resistant binders and agglomeration procedures developed in this project will also be adapted for use in improving the energy efficiency and performance of a broad range of mineral agglomeration applications, particularly heap leaching. The active involvement of our industrial partners will help to ensure rapid commercialization of any agglomeration technologies developed by this project.

Table of Contents

List of Tables and Figures

Introduction

The high grade ores which were once easily mined have become depleted. This means it is necessary for ore to be ground to a finer particles size in order for it to be liberated. The finer-grained ores is much harder to handle, and is not producing the required recoveries with the current operating conditions. Agglomerating the material into pellets, similar masses, or particles that are durable enough to be handled, is a solution to dealing with these fine mineral concentrates. Thus, allowing them to be more easily processed to extract the valuable minerals at lower costs. Agglomeration is important in the heap leaching of metals such as gold and copper as it increases the availability of transport of the leach solutions throughout the heap.

Heap leaching of copper sulfide minerals requires the ability for solution with dissolved iron to maintain access to the ore particles. It also requires easy flow of air to provide oxygen. The geometry of the leaching operation consists of crushing the ore to an appropriate size (typically a top size of 0.5 inches) and conveying into an agglomeration drum where it is wetted with raffinate (barren leach solution). Sufficient raffinate is added to make the ore into an adhesive mass, but not enough to convert it into a plastic or fluid mud. The moistened ore is tumbled in the drum and the smaller particles adhere to the larger particles. This agglomerated ore is transported to a pad and placed on top of an aeration system to a set height known as a lift (lift heights vary from mine to mine, but approximately 20 feet is typical). The lift is irrigated with raffinate either by drip emitters or a sprinkler system. The raffinate is then percolated through the heap and air is blown from the bottom allowing the copper to be dissolved from the ore. The solution, now referred to as PLS (pregnant leach solution), is captured in a pond. It is then sent to a solvent extraction and electro winning circuit where the liberated copper is ultimately recovered.

During the leaching cycle the agglomerates break down rapidly, and fines begin to migrate. The migration of fines clog flow channels through the ore in the heap leaving areas in the heap void of the necessary reagents to dissolve the copper resulting in lower recoveries that what is expected. A cost effective binding agent in the agglomeration step could greatly enhance the overall recovery of the heap by preventing agglomerate breakdown and limiting the migration of fines. In addition, the use of a proper binding agent should result in a more uniform percolation throughout the heap, which may also shorten leach cycles allowing production to increase. The problem with copper leaching is that it requires a high use of acid solutions which decrease the pH of the heap to very acidic conditions. Most agglomeration binders which are used successfully in other operations require a more neutral or alkaline pH. Acid-resistant binders are needed for these copper operations which will not breakdown in acid, allowing access of air and leach solutions to reach the ore particles.

Executive Summary

The objective of this project is to develop and implement binders and agglomeration procedures that will increase the efficiency of heap-leaching operations. This is particularly important in copper leaching operations, where the acidic leaching environment prevents existing leaching binders from working satisfactorily. To prevent agglomerate breakdown from occurring, a binder is needed to attach the particles in the agglomerates together. This is done very successfully in many precious metal leach operations, where the use of an alkaline leaching solution makes it possible to use Portland cement and similar materials as binders. (McClelland, 1986; Chamberlin, 1986, Eisele and Pool, 1987). However, these cement-type binders dissolve readily in acid, and are completely ineffective in an acidic leaching environment. To date, no binders have been developed that are both effective in an acidic environment, and sufficiently economical to be used on a full industrial scale.

The goal of this project is to develop binders for mineral agglomeration that meet these requirements, allowing for increased processing efficiency. Binders are being developed based on theoretical considerations and on past experience, and are being evaluated to determine their effectiveness in an acidic leaching environment. Three tests have been developed to determine the quality of a binder to be used in agglomeration in the heap leaching process. These tests are the soak test, flooded columns, and long-term leach columns. The soak test consists of immersing agglomerated ore in an H_2SO_4 solution and observing the degree of breakdown of the agglomerates with time. The flooded columns give quantitative measurements of the permeability of the ore to the leach solution as a function of time, and also provide a measure of the "slump" of the ore. The long-term leach columns simulate as closely as possible the conditions seen in their industrial leaching heaps. It is emphasized that these testing procedures are still not yet confirmed. Duplicate testing is currently being run to verify the accuracy of these testing processes.

The soak test and flooded columns along with the calculations of fines migration, bulk density, and hydraulic conductivity were some factors that went into narrowing down the field of binders to a select few that will be tried in the long-term leach columns.

Six long term leach columns have been arranged to test the long-term effects of binder usage on copper recovery rates. After reviewing the results from the soak tests and flooded column tests performed at Michigan Technological University (MTU), Phelps Dodge, Inc. assigned an internal project to their research facility. This project will enable Phelps Dodge to progress with additional larger scale test work while staying aligned with MTU. Currently, six long-term leach columns are being evaluated at Phelps Dodge's Process Technology Center (PTC) in conjunction with MTU. Both locations are collecting data on the analysis of the pregnant leach solution which includes pH, temperature, iron recovery, copper recovery, free acid content, and oxidation/reduction potential. The two sets of columns, one run at Michigan Tech, the other at Phelps Dodge PTC, will be able to be compared for reproducibility. The final results from these columns will also indicate if further experimentation in a test heap at the Phelps Dodge facility would be valuable.

A total of six large long-term leach columns have been started. The ore was sent from Phelps Dodge Process Technology Center (PTC) in approximately 80-lb charges. Ore assays were also completed by the PTC. The six columns will be filled with non-agglomerated ore, ore agglomerated with raffinate only, the third will have ore agglomerated with Binder B, the fourth with Binder A, the fifth with ore agglomerated with Binder C, and finally the sixth will have ore agglomerated with Binder D.

Compaction which occurs due to the weight of the ore in the heap may be partially responsible for the ponding, blinding, and solution channeling which are found within these heaps. Compaction causes a breakdown of the agglomerates which leads to an increased bulk density and therefore decreased void space. The decrease in void space makes it difficult for solution to flow through the heap. The migration of fines in these compacted areas leaves dead zones in which solution cannot flow, leaving them un-leached. Testing methods are being developed to investigate the effects of compaction on copper recovery rates.

Industrial cost-share for this project is being provided by Phelps Dodge, Inc., Newmont Mining Co., and Northshore Mining Co. All three companies have already contributed considerable amounts of engineering time to this project, and Phelps Dodge has provided experimental apparatus for conducting flooded and column leaching tests. Phelps Dodge has also provided several hundred pounds of their Mine for Leach (MFL) ore, and will provide additional ore as needed in the project.

Industrial Involvement

After reviewing the results from the soak tests and flooded column tests performed at Michigan Technological University (MTU), Phelps Dodge, Inc. assigned an internal project to their research facility. This project will enable Phelps Dodge to progress with additional larger scale test work while staying aligned with MTU.

A roundtable meeting between Michigan Technological University and the Phelps Dodge Industrial Team was held to discuss many issues revolving around the results, collected from the soak tests and flooded column tests, by Michigan Tech. The Phelps Dodge Industrial Team was comprised of the hydrometallurgical manager at their Bagdad facility, and the research engineer and lead research technician whom were assigned to the internal Phelps Dodge project. Issues were discussed such as the test work being run at Michigan Tech and the Process Technology Center, along with the complexities which our industrial partners would like to see addressed in order to implement MTU's ideas on an industrial scale.

Every month a report is written by Michigan Tech to update Phelps Dodge on the status of the project. This report is distributed throughout all of the Phelps Dodge locations. Bi-weekly communication is also often made between the Phelps Dodge employees and the Michigan Tech researchers. Although there is close communication between the

University and industry, this meeting gave the opportunity to communicate in person with the Phelps Dodge team. The involvement of our industrial partners will help to ensure rapid commercialization of any agglomeration technologies developed by this project.

Experimental

Materials

200 lb of Mine for Leach (MFL) Ore was received from the Phelps Dodge Morenci operation for use in soak tests and flooded column tests. This ore was crushed to pass ¼ inch in order to be a suitable size for agglomeration tests, and was then divided using a rotary sample splitter to ensure that all samples used in experiments had identical size distributions and compositions. An analysis of the raffinate composition at the Morenci operation was provided, and a simulated raffinate solution was prepared that contained all of the elements that were present at concentrations greater than 100 ppm, which are shown in Table 1. These elements were added as sulfate salts, along with sufficient sulfuric acid to simulate the Morenci raffinate:

Table 1: Composition of Simulated Raffinate.

Elements	Al	Ca	Cu	Fe	Mg	Na	Zn	SO_4^{-2}
Concentration (mol/l)	0.254	0.013	0.004	0.056	0.089	0.000869	0.0244	0.0612

Two 350 gallon totes of industrial raffinate were received from Phelps Dodge. This raffinate was drawn directly from their process lines and will be used in the long-term leach test columns. It will also aid in the simulation of the industrial leaching heaps. The results of the chemical analysis are shown in Table 2. As you can see, these results are similar to the simulated raffinate which had been used prior to receiving the industrial raffinate.

Table 2: Composition of Industrial Raffinate.

Elements	Al	Ca	Cu	Fe	Mg	Na	Zn
Concentration (mol/l)	0.299	0.016	0.005	0.050	0.107	0.000742	0.0271

Equipment

Soak Tests

The soak tests help look at how well the agglomerates hold together after being agglomerated with various binders. A Tyler 10 mesh screen is used as a base for the agglomerates while they are being immersed in a sulfuric acid solution. The fines which pass through the 10 mesh screen can then be collected. A screen and fines are shown in Figure 1.

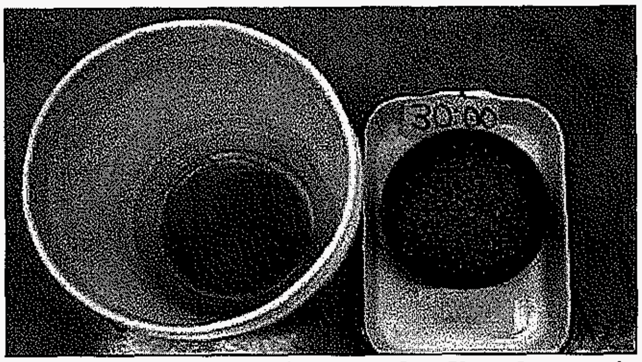

Figure 1: On the right is the 10 mesh screen holding the previously immersed agglomerates. The bucket on the left contains the fines which have been released due to the breakdown of the agglomerates.

Flooded Columns

The flooded columns have been designed to help analyze the effects of various binders on a slightly smaller scale. These columns, shown below in Figure 2, were assembled using equipment provided by Phelps Dodge Inc. Each column has an inside diameter of 3 inches, and a height of 20 inches. The raffinate is held in a container at the base of the columns, and is pumped up to the top where it drips onto the surface of the ore, slowly filling the columns. The solution passes through the ore and into a flask where any fines passing through the column can be collected.

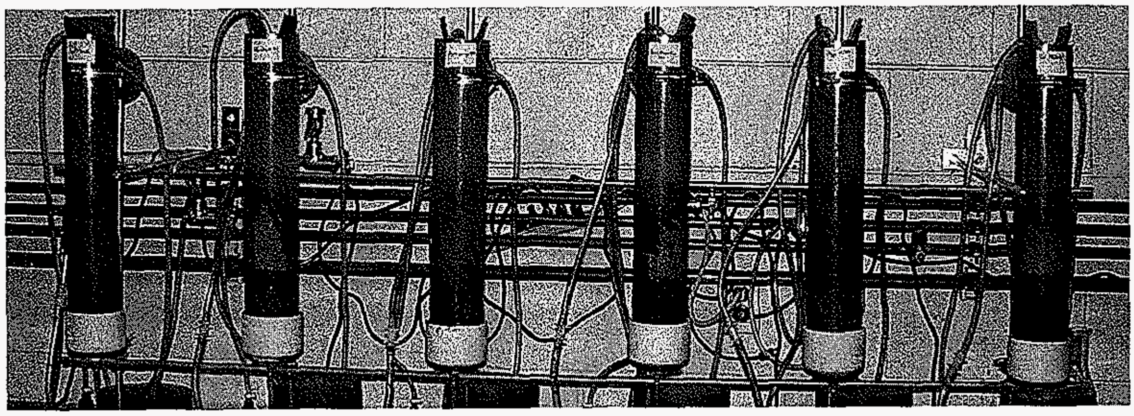

Figure 2: Flooded test columns assembled at MTU using equipment provided by Phelps Dodge Inc. Agglomerated ore is added to the column, and raffinate is circulated through the agglomerates continuously. The "slump", or decrease in height of the ore, is also measured. The columns shown each contain agglomerates made with a different binder, and were initially all filled with the same amount of ore.

Long-Term Leach Columns

The long-term leach columns have been assembled to simulate the heap leaching process occurring at the Morenci location of Phelps Dodge Inc. The columns, shown below in Figure 3, were created out of materials received from Phelps Dodge. Our laboratory houses six large PVC columns. These columns are approximately 5 ft in height with an inside diameter of 5.89 in. Each column has recently been equipped with an air flow meter which injects air into the lower part of the column, and a cover containing an air trap. Raffinate is held in the side containers and is pumped into the top of the columns. It then percolates through, and the pregnant leach solution is then collected in the buckets below.

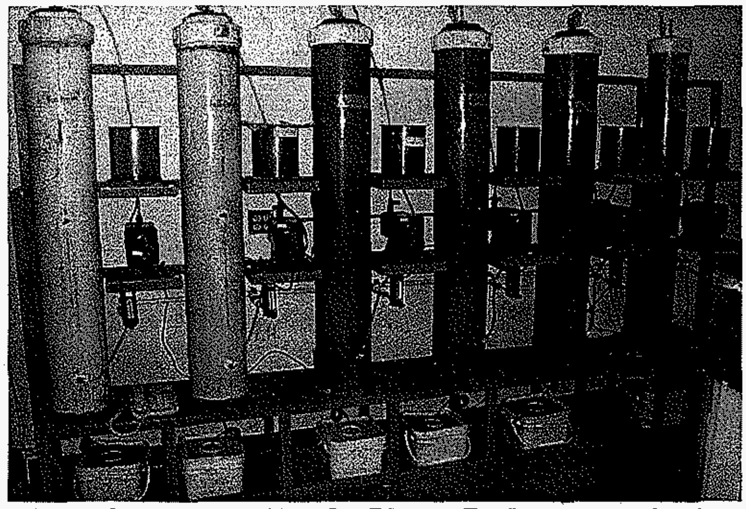

Figure 3: Leaching columns, provided by Phelps Dodge, set up for leach testing at Michigan Technological University. These columns are used for long-term testing for periods of several months, and provide the closest simulation of actual industrial heap-leaching behavior that can be achieved in the laboratory.

<u>Test Procedures</u>

The soak test is the first analysis which is performed on a binder. Approximately 500 grams of ore are used in this test. The ore is agglomerated in a rotating drum with raffinate and the binder over a period of 20 minutes. The ore is then transferred to a Tyler 10 mesh screen and allowed to air dry or cure overnight, or for approximately 24 hours. The screen is then lowered into a 6 g H_2SO_4/L water solution and left to sit from 30 minutes. After 30 minutes, the screen is carefully removed. The acid solution is decanted, and fines passing through the screen are collected, dried, and weighed. The procedure is diagramed in Figure 4.

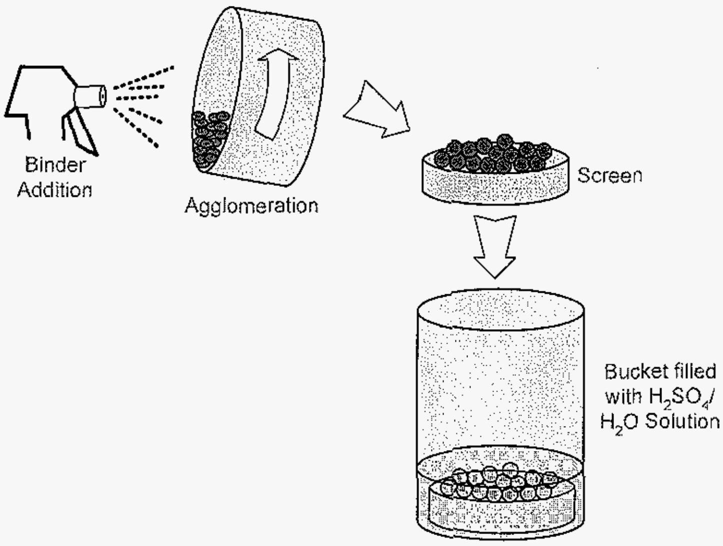

Figure 4: Schematic of Agglomerate Soak Test.

To further test the selected polymer, a flooded column test is performed. Two kilograms of ore is agglomerated with raffinate and the binder. After being dried to a1% moisture, the ore is then transferred to a 3 inch diameter column. Raffinate solution is dripped onto the ore at the top of the column where it fills the columns. The solution exits the column through the overflow system. Figure 5, below, outlines this process. The mass of particles which are collected is a measure of the degree of fines migration that occurs with a given binder. In addition, the height of the agglomerated ore is measured as a function of time. This "slump" measurement is a direct measure of the degree of agglomerate breakdown. The hydraulic conductivity can be calculated by measuring the flow rate and hydraulic head in the column.

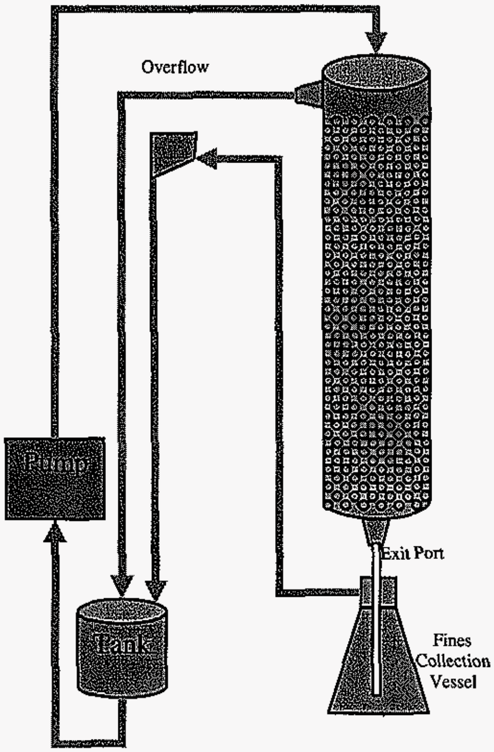

Figure 5: Schematic of Flooded Test.

The best binders will then be tried in the long-term leach columns, as the leach cycle for these columns is 150 days. Here approximately 80 lbs of material is agglomerated with raffinate and a selected binder, in an agglomerating drum. It is then spread out to air dry, or "cure" for at least 48 hours. The dry agglomerates are transferred to the column. The column is capped with a cover containing an air trap. The raffinate is pumped to the top of the column at a flow rate of 27.9 ml/hour. This rate was determined by the rate being used at the plant, scaled down appropriately to these equipment sizes. At this time air is also being injected into the bottom of the column at a flow rate of 16.68 ml/min. The raffinate solution percolates slowly through the column, and is collected in a bucket below, as shown in Figure 6. The solution collected is called the pregnant leach solution (PLS), and is later tested for copper and iron recovery along with free acid, pH, oxidation/reduction potential (ORP), and temperature.

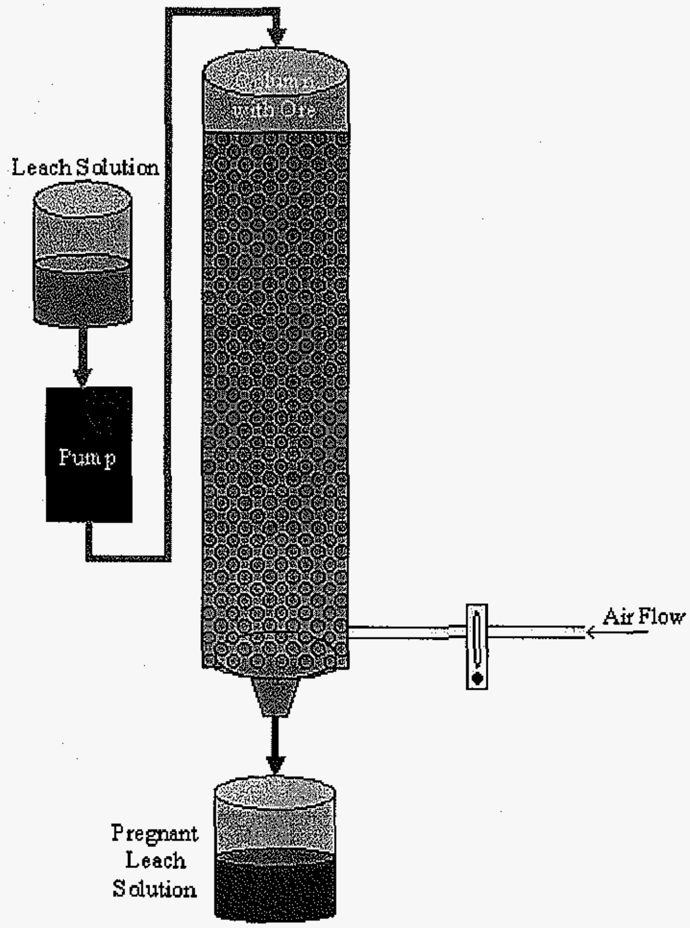

Figure 6: Schematic of Leach Testing Column

Calculations

The bulk density can be calculated from the measurements taken in the flooded columns. It can be calculated using Equation 1.

$$\rho_{Bulk} = \frac{weight\ of\ ore}{volume\ of\ ore} \tag{1}$$

Equation 1 can be re-written for the laboratory columns shown in Figure 7, resulting in Equation 2.

$$\rho_{Bulk} = \frac{m_{ore}}{\pi * \left(\frac{D}{2}\right)^2 * (50.8 - y)} \tag{2}$$

Where:

- m_{ore} = dry mass of ore (g)
- D = inner diameter of column (cm)
- y = distance from top of the column to top of the ore bed (cm)
- L = height of ore bed (cm)

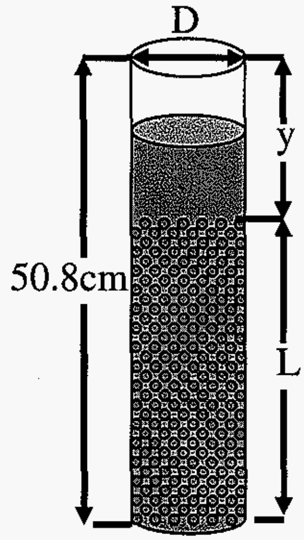

Figure 7: Experimental Parameters for Bulk Density Calculation

The change in bulk density, Equation 3, is reported rather than reporting either the final or initial bulk densities. Reporting the change eliminates differences due to variables such as differences in agglomerate size or differences in column loading.

$$\Delta\rho_{Bulk} = \rho_{Bulk\ Final} - \rho_{Bulk\ Initial} \qquad (3)$$

Hydraulic Conductivity can be determined using Darcy's Equation defined in Equation 4 to define the flow of a solution through a porous medium. Darcy's Equation often represents a system as diagramed in Figure 8. The same equation can be used to define the laboratory columns used, using the parameters in Figure 9. The system must be in equilibrium, Equation 5, for Darcy's Law to be valid for this experiment.

$$Q = A * K * \frac{\Delta h}{L} \qquad (4)$$

Where:

- Q = volumetric flow rate (m^3/s)
- L = flow path length (m)
- A = flow area perpendicular to L (m^2)
- Δh = change in hydraulic head (m)
- K = hydraulic conductivity (m/s)

$$Q = Q_{In} = Q_{Out} \qquad (5)$$

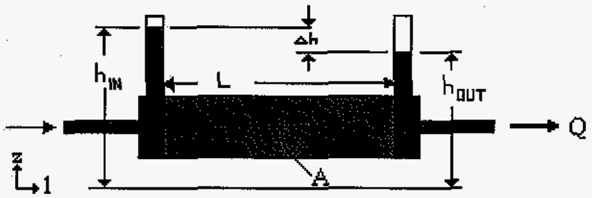

Figure 8: Parameters for Darcy's Law Applied to a 1-Dimentional Flow in a Simple Column Flow in a Simple Column
http://biosystems.okstate.edu/darcy/LaLoi/basics.htm

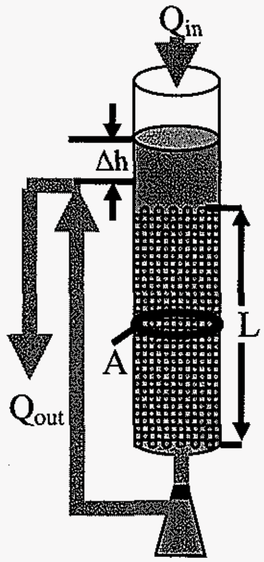

Figure 9: Parameters for Darcy's Law Applied to Laboratory Scale Columns

The area (A) is the only variable which is held constant in the experimental calculations. All the other variables are directly measured to acquire each data point for hydraulic conductivity.

Results and Discussion

The development of the soak test, flooded columns, and long-term leach columns are still being refined. Testing will always be replicated performed to analyze the accuracy of these tests.

A one month long-term leach column has been completed. This column served as a trial run, indicating any problems or concerns which should be addressed before beginning the 150 day leach cycle. The 81.5 pounds of ore in this column was agglomerated with raffinate only. The ore was leached for a total of 41 days, and 14 samples were taken during this period. The first sample of PLS was taken from the bottom of the column after eight days.

It was found that the current agglomeration drum did not have the motor capabilities to hold the 81.5 pound load required. The motor was then repaired along with other gear fixtures on the drum, leaving it in working order.

Initially, the ore used for this test contained 177.7 grams of copper which was available to be leached. Within the 41 days of leaching a cumulative copper recovery of 61.9% was reached, shown in Figure 10.

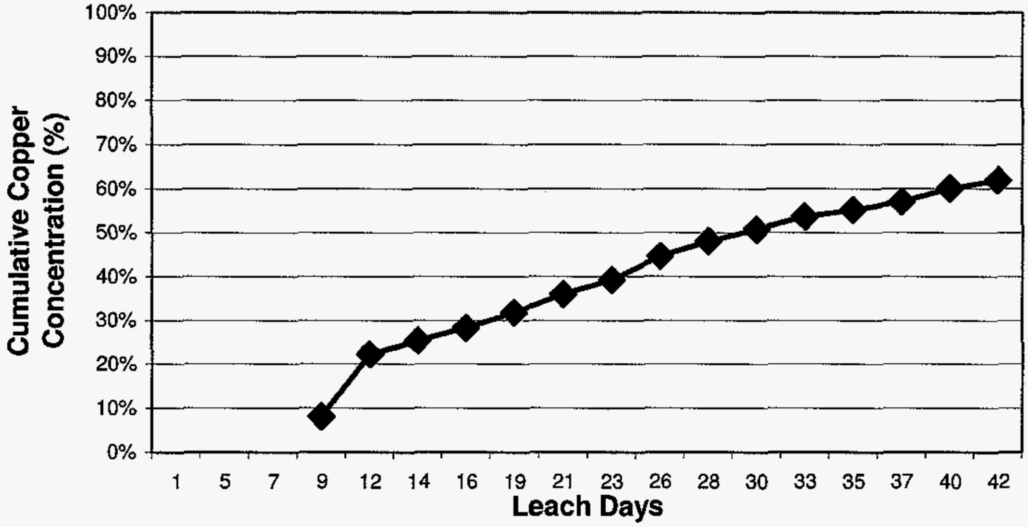

Figure 10: Cumulative Percent Recovery of Copper in the One Month Long-Term Leach Columns

The rate of recovery of copper within this system is unusually high for the short period of time in which the column was under operation. The increased copper concentration in the product solution may be due either to a low initial copper grade or to small errors while analyzing product solutions using the atomic adsorption (AA) spectrometer. Extremely high dilution factors needed to be used, leaving room for any small error to be multiplied considerably, possibly leading to the impression that more copper was being recovered than what was actually present.

The oxidation/reduction potential (ORP), pH, and temperature were three of the other parameters, aside from copper concentration, which were measured during this test period. The results of these measurements are given in Figures 11 and 12. The ORP increased over the sampling period with a decrease in pH and under a relatively constant temperature.

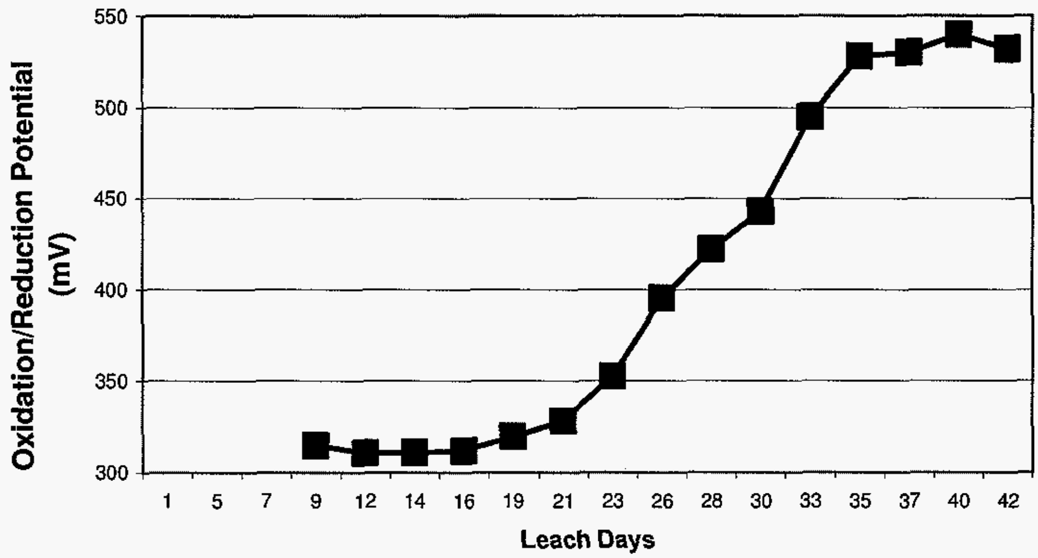

Figure 11: Oxidation/Reduction Potential of the PLS Collected From the One Month Long-Term Leach Columns

The pH of the PLS decreased over the sampling period while the system remained at a constant temperature.

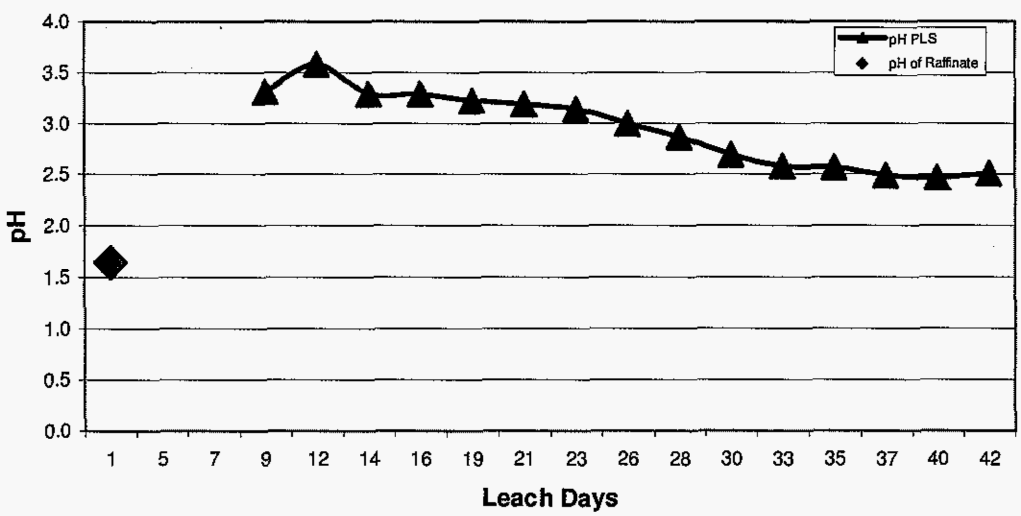

Figure 12: pH of the PLS & Raffinate Solutions Used in the One Month Long-Term Leach Columns

Minor problems associated with the long-term leach columns were observed and corrected. However, before the columns can be used, the optimal binder addition rates need to be determined. To accomplish this, multiple flooded columns were run at various binder addition rates.

Before the long-term leach columns can be implemented for testing binders, each binder dosage rate needed to be optimized. The optimization of the binder addition rate was completed using the flooded column test. The flooded columns address the two issues of void space and hydraulic conductivity. The void space within an ore body is important to obtain optimum kinetics of the leaching process by providing the area necessary for good liquid and gas interface. The hydraulic conductivity, or the ability for solution to flow freely through the heap, ensures reagents can be carried through the heap easily allowing for better kinetics. A good binder used for agglomeration addresses these issues by keeping fines bound together creating a more uniform size distribution.

Four binders, Binder A, B, C, and D, were optimized using bulk density and hydraulic conductivity measurements.

The optimum dosage for Binder A lies around the 5 lb/ton addition rate. The optimum dosage is determined by looking at the binder dosage rate when the hydraulic conductivity first beings to reach a state where there is no longer a significant increase in hydraulic conductivity with increasing binder addition, shown in Figure 14.

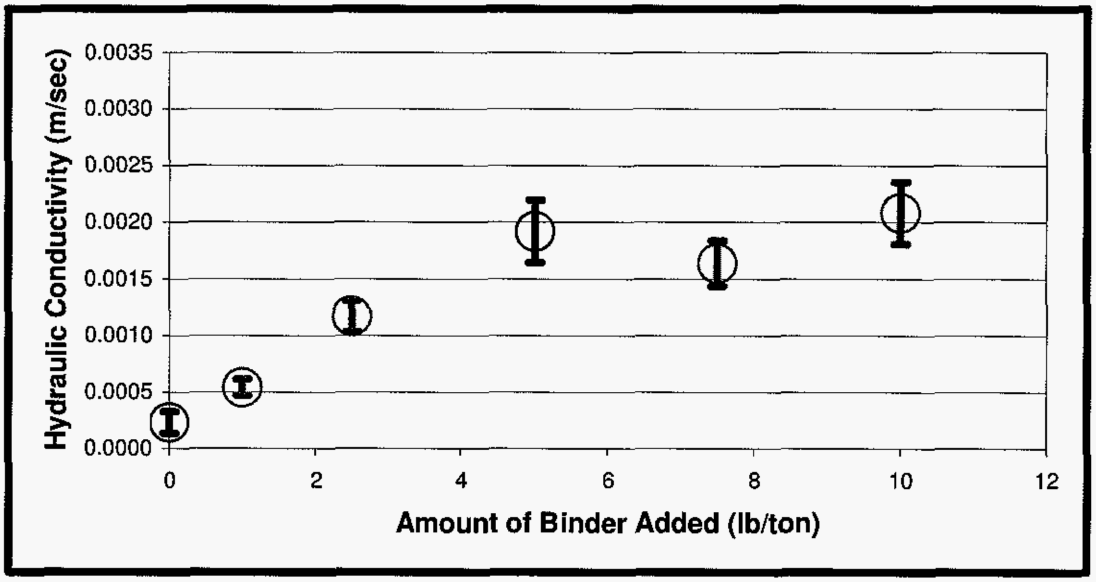

Figure 14: Flooded Column Hydraulic Conductivity Evaluation for Binder A

The change in bulk density also shows a leveling trend around the 5 lb/ton dosage rate, shown in Figure 15.

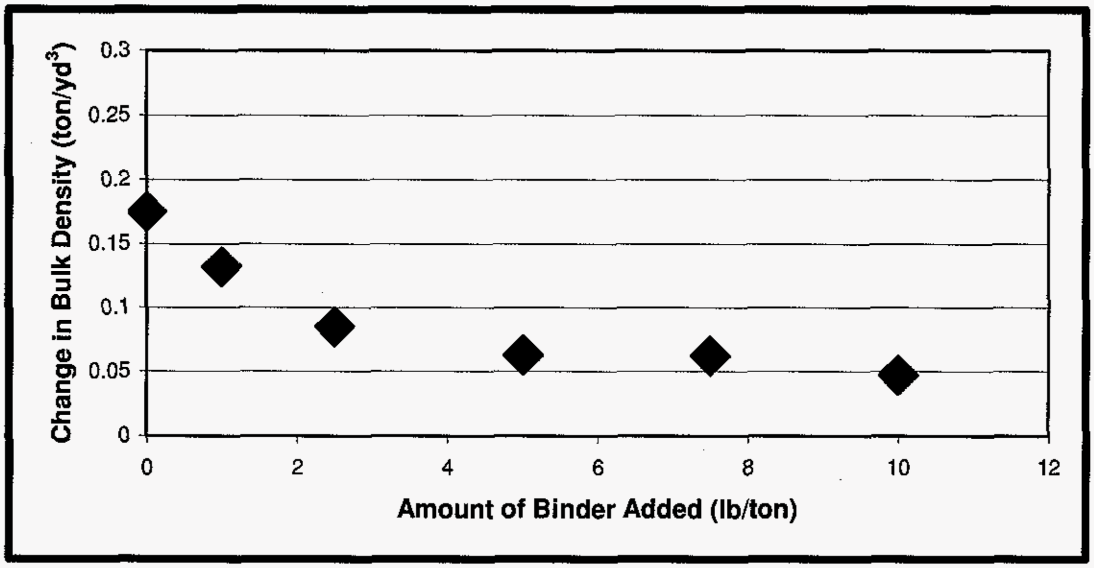

Figure 15: Flooded Column Bulk Density Evaluation for Binder A

The optimum dosage rates were determined for all four binders. After the optimum dosage rates were determined using the hydraulic conductivity and bulk density data, the six month-long columns were started. These columns included a column filled with non agglomerated ore, a column with ore agglomerated with raffinate only, and finally the remaining columns will each be loaded with ore agglomerated with either Binder A, B, C, or D.

Future and Continuing Test Work

Six month-long columns are being run using the optimized dosage values found while completing the hydraulic conductivity and bulk density work. These columns are being run at the Phelps Dodge Process Technology Center under the conditions provided to them by Michigan Tech. The columns include a column filled with non agglomerated ore, a column with ore agglomerated with raffinate only, and finally the remaining columns will each be loaded with ore agglomerated with either Binder A, B, C, or D.

Currently, all the ore is being added to the flooded columns with only 1% moisture. It has been noted that Binder B, especially, performs better with less moisture. Therefore, Binder B needs to be analyzed for its performance when agglomerates being added to the flooded columns have greater than 1% moisture, as this may more closely represent what would occur in a heap.

Test work is currently underway to evaluate the binders under compression. This test work is being performed with a flooded column like set up. A newly built apparatus maintains a constant weight applied to the top of the agglomerated ore throughout the 24-hr long test. During this time, data is taken so hydraulic conductivity and bulk densities can be calculated. These numbers have been used to compare the different binders. This will give a better understanding of the additional benefits of each binder in a heap leach setting.

Three columns have currently been run, one with non agglomerated ore, the next using Raffinate as a binder, and the third using a synthetic binder. The Raffinate and the synthetic binder columns have both been run in triplicate.

Comparison of the results shows a large increase in the evenness of solution flow throughout the ore bed with the use of a synthetic binder. Channeling occurred when testing the non-agglomerated ore and the ore with Raffinate as a binder. The hydraulic conductivity data gives indication as to when the channels are formed, and the use of a tracer helped to confirm the location of the channels in the column. The amount of fines migration in the raffinate column was more than 10 times the amount collected from the synthetic binder column. Overall, the impact of compaction is large and can be seen when comparing the flooded column results under compaction to the flooded column results when compaction in not taken into consideration.

Conclusions

Agglomeration of copper sulfide ore for heap leaching critically requires a binder, as binderless agglomerates break down rapidly and completely on contact with acidic leaching solution. Based on soak test and flooded column results, it is evident that polyacrylamide polymers are effective as binders, and will continue to be further evaluated. Additional binders, particularly organic polymers, have been selected based on their expected behavior in acid solutions.

Of the numerous binders examined, four have proven to perform well in both the soak test and flooded-column flooded tests. They prevent disintegration of agglomerates in acid solution, suppress fines migration and maintain a low bulk density and high hydraulic conductivity in the agglomerated ore. The optimum dosage rates for these binders have been determined, and are being evaluated in the long-term leaching column tests at Michigan Technological University in conjunction with the Phelps Dodge Process Technology Center. Binder addition rates need to be analyzed to find an optimum balance between performance and cost for each binder.

Communication with Phelps Dodge will continue in order to keep moving the project in a commercially driven direction. Results from both locations will be compared in order to determine the best course of action.

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